

# The QMFF-Cx forcefield for carbon validated to reproduce the mechanical and thermodynamics properties of Graphite

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Supplementary Materials

## TABLES

**Table S.I.** Experimental structural and elastic properties of Graphite.

	300K <sup>a</sup>	300K-> 0K <sup>b</sup>	0K
<b>Lattice Parameters (Å)<sup>c</sup></b>			
$a$	2.4612	0.0072	2.4684
$c$	6.7090	-0.0369	6.6721
<b>Elastic Constants (GPa)</b>			
$C_{11}$	1060±20	66±8	1126±22
$C_{12}$	180±20	20±2.5	200±20
$C_{33}$	36.5±1	4.2±0.5	40.7±1.1
$C_{44}$	4.5±0.5	0.01±0.001	4.51±0.5
$C_{13}$	15±5	23.8±40	39.5±40
<b>Young's Moduli (GPa)</b>			
$E_1$	1020±30		
$E_3$	36.5±1.0		
<b>Poisson Ratios</b>			
$\mu_{21}$	0.16±0.06		
$\mu_{31}$	0.34±0.08		
$\mu_{13}$	0.012±0.003		

<sup>a</sup> See Donohue<sup>15</sup> and Blakslee et al.<sup>17</sup>

<sup>b</sup> See Bailey and Yates<sup>16</sup> and Gauster and Fritz<sup>24</sup>

<sup>c</sup> 298K was used instead of 300K

**Table S.II.** Charges (e<sup>-</sup>) on the PD-X orientation of the DHC dimer at equilibrium, determined using three different charge schemes. The 6-311+G(2d,2p) basis set was used. These values are compared to that of the coronene dimer, reported in Ref<sup>28</sup>. We selected the ESP charges on the dimer when fitting to QMFF-Cx forcefield.

Atom <sup>a</sup>	Monomer			ΔDimer <sup>b</sup>		
	Mulliken	ESP	CM4 <sup>c</sup>	Mulliken	ESP	CM4
<b>C1</b>	-0.0071	-0.0025	0.01	0.0035	0.0026	0.004
<b>C2</b>	-0.0500	0.0120	-0.01	0.0027	0.0030	0.004
<b>C3</b>	0.0281	-0.0048	-0.07	0.0031	5.0x10 <sup>-5</sup>	0.007
<b>H</b>			0.07			0.003

<sup>a</sup> C1 – 6 carbons of the innermost benzene ring, C2 – 6  $sp^3$  carbons not bound to H atoms, C3 – remaining 12 outermost carbons (bound to H atoms in the case of coronene)

<sup>b</sup> Average dimer charges of the PD-X configuration at the interaction minima ( $\Delta x = 1.45\text{Å}$ ,  $\Delta z = 3.408\text{Å}$ )

<sup>c</sup> As reported in Ref.<sup>28</sup>

<sup>d</sup> Absolute value of change in dimer charge was reported

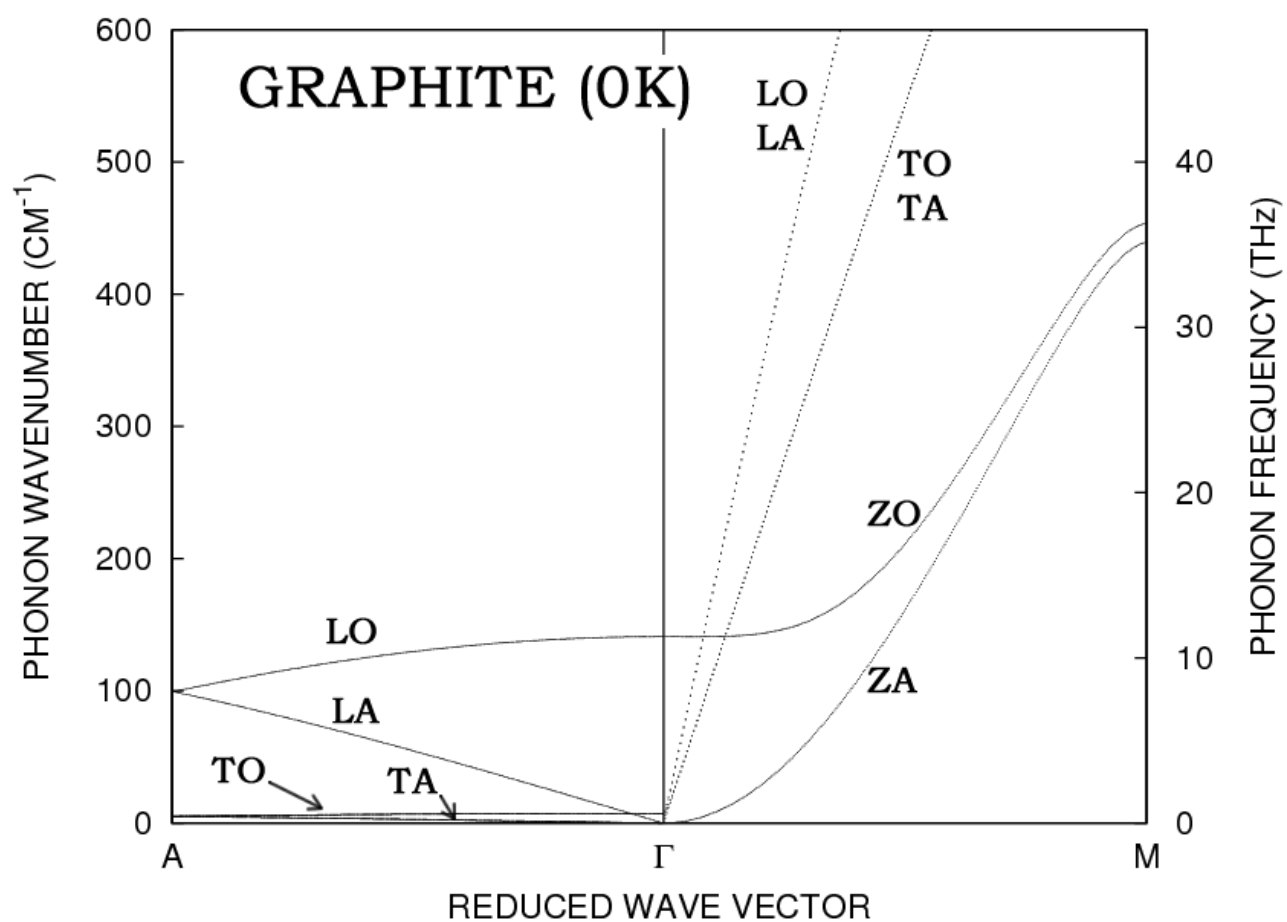
**Table S.III.** Comparison of binding energies (kcal/mol) with and without counterpoise corrections (cp) of DHC using various basis sets. Singlepoint calculations were performed at the equilibrium geometry obtained from 6-311G+(2d,2p) optimization. The calculated graphite cohesive energy is obtained by fitting the energies and forces of the PD-X structure to a LJ 12-6 potential. The convergence criteria were  $5 \times 10^{-5}$  Hartree for the energy and  $5 \times 10^{-6}$  rms for the density matrix.

	# basis funcs	PD-X		PD-Y		Eclipsed		<sup>a</sup> E <sub>coh</sub>
		ΔE	ΔE <sub>cp</sub>	ΔE	ΔE <sub>cp</sub>	ΔE	ΔE <sub>cp</sub>	
<b>Pople</b>								
6-31G(2,p)	720	-19.43	-13.94	-18.75	-13.39	-11.48	-6.79	-0.99
6-311G(2d,2p)	864	-20.04	-15.03	-19.18	-14.12	-12.12	-8.26	-1.07
6-311G(3df,3pd)	1680	-21.45	-16.93	-22.76	-18.00	-13.31	-9.28	-1.16
<b>Pople + diffuse</b>								
6-31+G(2,p)	912	-20.50	-15.28	-19.58	-14.81	-12.13	-7.12	-1.09
6-311+G(2d,2p)	1056	-22.10	-16.73	-21.29	-16.07	-15.06	-10.68	-1.20
6-311+G(3df,3pd)	1872	-23.81	-18.08	-22.20	-16.53	-16.78	-12.02	-1.35
<b>Dunning</b>								
cc-pvdz(-d)	432	-23.78	-19.82	-22.87	-19.20	-15.41	-12.91	-1.43
cc-pvdz	672	-21.85	-17.78	-20.92	-17.34	-14.34	-11.07	-1.28
cc-pvtz(-f)	1104	-20.73	-17.67	-20.03	-16.95	-12.81	-10.19	-1.27
cc-pvtz	1440	-20.39	-17.34	-19.48	-16.40	-12.10	-9.22	-1.17
cc-pvqz(-g)	2208	-18.07	-16.89	-17.88	-16.36	-10.70	-9.66	-1.11
<b>Dunning + diffuse</b>								
cc-pvdz(-d)+	624	-25.31	-19.01	-24.53	-18.30	-17.01	-10.82	-1.37
cc-pvdz+	1104	-22.49	-18.59	-21.81	-17.96	-15.12	-11.37	-1.34
cc-pvtz(-f)+	1536	-20.71	-17.90	-21.10	-18.07	-13.92	-11.20	-1.29
<b>MIDIX</b>	432	-30.77	-19.71	-29.84	-18.93	-20.25	-9.99	-1.42

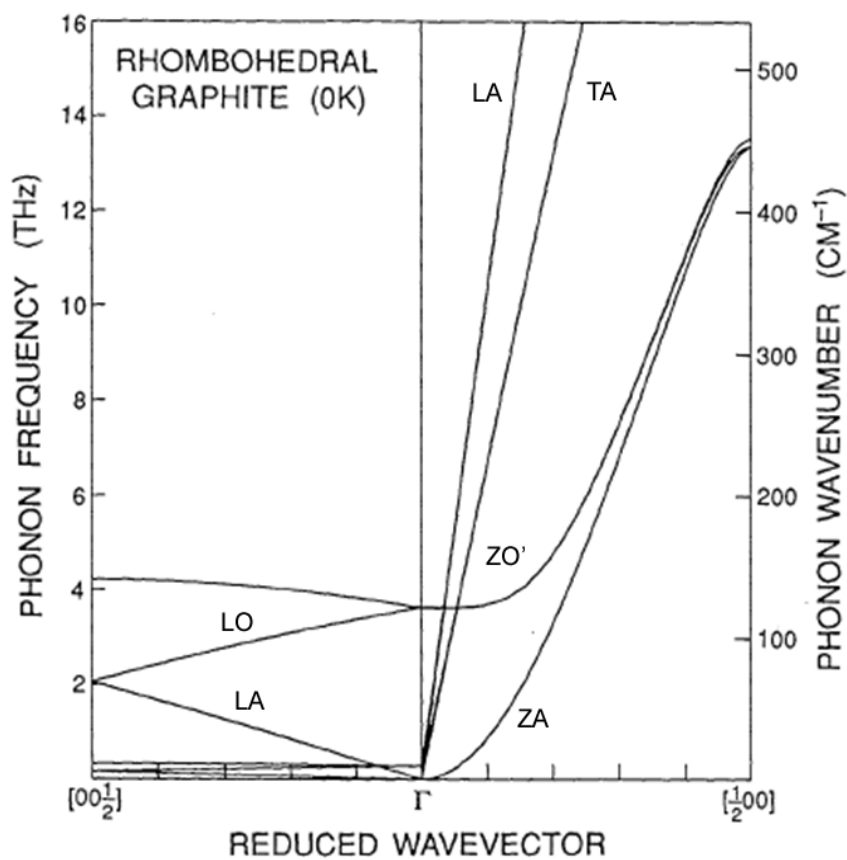
<sup>a</sup> experimental cohesive energy of graphite is  $1.19 \pm 0.15$  kcal/mol



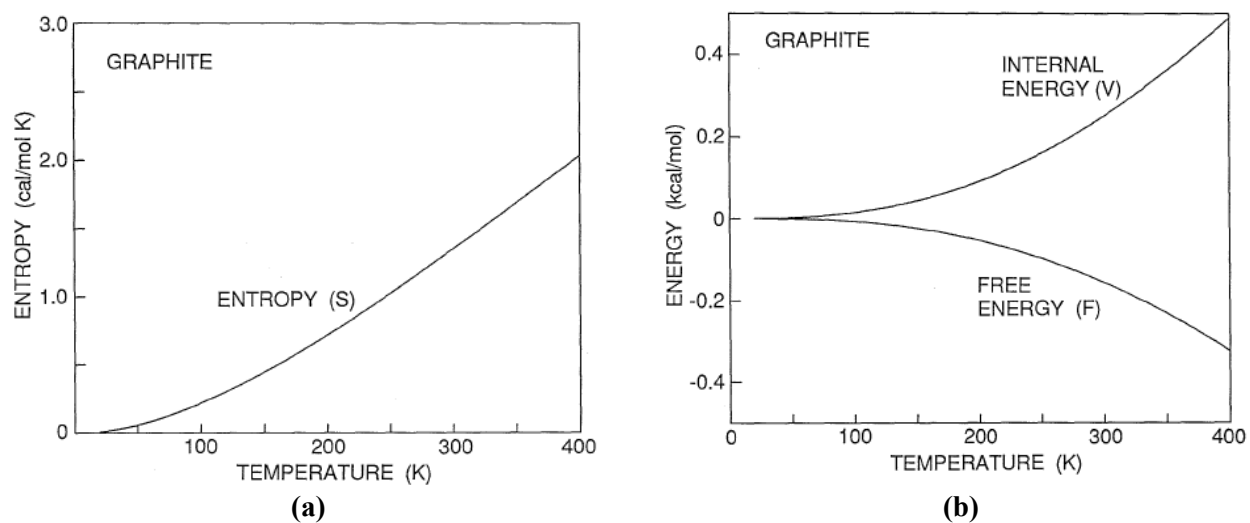
# FIGURES



**Figure S.1.** Phonon dispersion curve for low frequency modes of (hexagonal) graphite at 0K



**Figure S.2.** Phonon dispersion curves for the low frequency modes of rhombohedral graphite at 0K (using the X6 potential)



**Figure S.3.** (a) Vibrational entropy (S) of graphite (b) Vibrational internal energy (V) and free energy (F) of graphite